

# Dielectric Properties of Continuous Media: The Lorentz-Debye-Sack Theory

## Ionic and Dipolar Solutes in Polar/Polarizable Solvents

Consider an **ion** or a **dipole** immersed into a solvent composed of molecules with isotropic polarizabilities  $\alpha$  and permanent dipole moments  $\mu$ . Regardless of its nature, the solute creates a field that orients and polarizes the surrounding molecules of the solvent. The Lorentz-Debye-Sack (LDS) theory of liquids relies on the following basic equations of electrostatics:

$$\mathbf{D}(\mathbf{r}) = \mathbf{E}(\mathbf{r}) + 4\pi\mathbf{P}(\mathbf{r}) \quad (1)$$

$$\mathbf{E}_l(\mathbf{r}) = \mathbf{E}(\mathbf{r}) + \frac{4\pi}{3} \mathbf{P}(\mathbf{r}) \quad (2)$$

$$\mathbf{P}(\mathbf{r}) = \frac{\alpha}{v} \mathbf{E}_l(\mathbf{r}) + \frac{\langle f(\Omega) \rangle}{v} \mu \quad (3)$$

where  $\mathbf{D}(\mathbf{r})$  and  $\mathbf{E}(\mathbf{r})$  are the displacement and the macroscopic (Maxwell) electric field at position  $\mathbf{r}$  in the solvent,  $\mathbf{P}(\mathbf{r})$  is the polarization at position  $\mathbf{r}$  in the solvent, and  $\mathbf{E}_l(\mathbf{r})$  is the local electric field acting on individual solvent molecules at position  $\mathbf{r}$ ;  $v$  is the molecular volume of the molecules of the solvent. In Eq.(3) the factor  $\langle f(\Omega) \rangle$  is the average of the orientation-dependent function of the solute-solvent interaction energy  $w$ , which depends on the source (i.e., ion or dipole)

Combining Eqs.(1) and (2) an expression for the local field is obtained,

$$\mathbf{E}_l(\mathbf{r}) = \frac{\varepsilon(\mathbf{r}) + 2}{3} \mathbf{E}(\mathbf{r}) \quad (4)$$

known as the Lorentz relationship. In the Debye-Sack approach to obtain  $\varepsilon(\mathbf{r})$ , Eqs.(1)-(3) are combined, to eliminate  $\mathbf{P}(\mathbf{r})$  and obtain the macroscopic fields  $\mathbf{E}(\mathbf{r})$  and  $\mathbf{D}(\mathbf{r})$  as a function of the local field  $\mathbf{E}_l(\mathbf{r})$  only:

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_l(\mathbf{r}) - \frac{4\pi}{3} \left[ \frac{\alpha}{v} \mathbf{E}_l(\mathbf{r}) + \frac{\langle f(\Omega) \rangle}{v} \mu \right] \quad (5)$$

$$\mathbf{D}(\mathbf{r}) = \mathbf{E}_l(\mathbf{r}) + \frac{8\pi}{3} \left[ \frac{\alpha}{v} \mathbf{E}_l(\mathbf{r}) + \frac{\langle f(\Omega) \rangle}{v} \mu \right] \quad (6)$$

### IONIC SOURCE:

For the case of an ion, the orienting function is given by  $f(\Omega)=f(\theta)=\cos\theta$ , where  $\theta$  is the angle formed by vectors  $\mathbf{r}$  and  $\mu$  (i.e.,  $\mathbf{r} \cdot \mu = r\mu \cos\theta$ ). The ion-

dipole interaction energy is given by  $w = -\mu E_l(\mathbf{r}) \cos\theta$  and, therefore, the Boltzman average yields  $\langle f(\mathbf{\Omega}) \rangle = \langle \cos\theta \rangle = L(\mu E_l(\mathbf{r})/kT)$ , where  $k$  is the Boltzmann constant and  $L(x) \equiv \coth(x) - 1/x$  is the Langevin function.

Combining Eqs.(4)-(6), using  $\mathbf{D}(\mathbf{r}) = \epsilon(\mathbf{r})\mathbf{E}(\mathbf{r})$ , and noting that, for an ion,  $\mathbf{E}(\mathbf{r}) = q\mathbf{r}/\epsilon(\mathbf{r})r^3$ , where  $q$  is the charge of the ion and  $\epsilon(\mathbf{r})$  is the dielectric function that characterizes the system at position  $\mathbf{r}$ , an implicit equation for  $\epsilon(\mathbf{r})$  is obtained that depends only on the distance  $r$  to the central ion, i.e.,

$$\epsilon(\mathbf{r}) = \epsilon(r) = 1 + \frac{4\pi}{3} [\epsilon(r) + 2] \frac{\alpha}{v} + \frac{4\pi\mu}{qv} r^2 \epsilon(r) L \left[ \frac{q\mu[\epsilon(r) + 2]}{3kTr^2 \epsilon(r)} \right] \quad (7)$$

Iterative or numerical solutions of this equation yield dielectric functions of the sigmoidal form (see below). An important observation is that, for pure solvent, the dielectric function  $\epsilon(r)$  is obtained from measurable quantities only, because the polarizability and dipole moment of the solvent are obtained from macroscopic measurements:

The Lorenz-Lorentz relationship connects the polarizability of the solvent molecules with the high-frequency dielectric constant  $\epsilon_\infty$  (or optical permittivity  $\epsilon_{opt}$ ; note that this relationship is more appropriate than the Claussius-Mossoti equation, that is valid only in the case  $\mu=0$ ), i.e.,

$$\frac{\alpha}{v} = \frac{3}{4\pi} \left[ \frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right] \quad (8)$$

On the other hand, far from the source Eq.(7) has to describe the static dielectric permittivity of pure bulk solvent  $\epsilon_s$  and, therefore,  $\mu$  is given by (note that  $L(x) \sim x/3$  as  $r \rightarrow \infty$ )

$$\mu^2 = \frac{27}{4\pi} kTv \frac{\epsilon_s - \epsilon_\infty}{(\epsilon_s + 2)(\epsilon_\infty + 2)} \quad (9)$$

### **DIPOLAR SOURCE:**

For the case of a dipole source the derivation above is conceptually similar but mathematically more cumbersome. If the source dipole is characterized by a permanent dipole moment  $\mu_s$ , the electric field is given by

$$\mathbf{E}(\mathbf{r}) = \frac{3(\mu_s \cdot \mathbf{r})\mathbf{r} - (\mathbf{r} \cdot \mathbf{r})\mu_s}{\epsilon(\mathbf{r})r^5}$$

where  $\mathbf{r}$  is the position of the center of  $\mu$  relative to the center of  $\mu_s$ . At any given instant, the interaction energy between the dipole source and the

dipole of a solvent molecule is  $w = -\mu\mu_s r^{-3} (2 \cos \gamma \cos \theta - \sin \gamma \sin \theta \cos \phi)$ , where  $\theta$  is the angle formed by vectors  $\mathbf{r}$  and  $\boldsymbol{\mu}$  (i.e.,  $\mathbf{r} \cdot \boldsymbol{\mu} = r\mu \cos \theta$ , as in the case of the ion above),  $\gamma$  is the angle formed by vectors  $\mathbf{r}$  and  $\boldsymbol{\mu}_s$  (i.e.,  $\mathbf{r} \cdot \boldsymbol{\mu}_s = r\mu_s \cos \gamma$ ) and  $\phi$  is the dihedral angle defined by both dipole moments, referenced to the vector  $\mathbf{r}$  that connects their centers.

In this case the calculation of  $\langle f(\boldsymbol{\Omega}) \rangle$  is not straightforward and a general analytical solution is difficult to obtain. Under the approximation of small dipole field,  $\langle f(\boldsymbol{\Omega}) \rangle = 2 \cos \gamma L(\mu E_l(\mathbf{r})/kT)$  and, as expected, the spherical symmetry that led to Eq.(7) now is broken and  $\varepsilon(\mathbf{r})$  depends on the position  $\mathbf{r}$  in the solvent. In many cases, measurements in real systems require a Boltzmann average to be taken also on all the orientations of the source dipole, i.e., on all possible angles  $\gamma$ . When this calculations is performed an expression similar to Eq.(7) is obtained, i.e.,

$$\varepsilon(\mathbf{r}) = \varepsilon(r) = 1 + \frac{4\pi}{3} [\varepsilon(r) + 2] \frac{\alpha}{v} + \frac{2\pi\mu}{\mu_s v} r^3 \varepsilon(r) L \left[ \frac{2\mu\mu_s [\varepsilon(r) + 2]}{3kTr^3 \varepsilon(r)} \right] \quad (10)$$

Although this equation is slightly different than Eq.(7), both dielectric functions are of the sigmoidal shape as it is discussed below, and its precise form can be obtained from physically measurable quantities only, with no adjustable parameters.

### **Reaction Field Effects**

Onsager noticed that the values of  $\mu$  of molecules in the liquid phase obtained from the LDS theory [cf.Eq.(9); note that the same expression is derived from Eq.(10)] were too small, even smaller than in the gas phase (e.g., for water it was calculated to be 0.82D, compared gas phase value of 1.87D) and attributed this problem to a misinterpretation of the effect of the local field  $\mathbf{E}_l(\mathbf{r})$ . Onsager proposed that only part of the local field created by a dipolar solute should be used to calculate the second average in  $\langle f(\boldsymbol{\Omega}) \rangle$ . Böttcher quantified this statement showing that the directing field  $\mathbf{E}_\Omega(\mathbf{r})$  is given by

$$\mathbf{E}_\Omega(\mathbf{r}) = \mathbf{E}_l(\mathbf{r}) - \mathbf{R}(\mathbf{r}) \langle f(\boldsymbol{\Omega}) \rangle \quad (11)$$

where  $\mathbf{R}(\mathbf{r})$  is the *reaction field*. Onsager showed that the reaction field can be expressed as

$$\mathbf{R}(\mathbf{r}) = \frac{4\pi}{3v} \frac{2(\varepsilon_s - \varepsilon_\infty)(\varepsilon_\infty + 2)}{2\varepsilon_s + \varepsilon_\infty^2} \frac{1}{3} \boldsymbol{\mu}_s \quad (12)$$

i.e., in this original approximation, it is independent of the position, although a local reaction field  $\mathbf{R}(\mathbf{r})$  at position  $\mathbf{r}$  can be defined by replacing  $\varepsilon_s$  by  $\varepsilon(\mathbf{r})$  in Eq.(12). After some algebra a corrected Eq.(10) is obtained that is given by

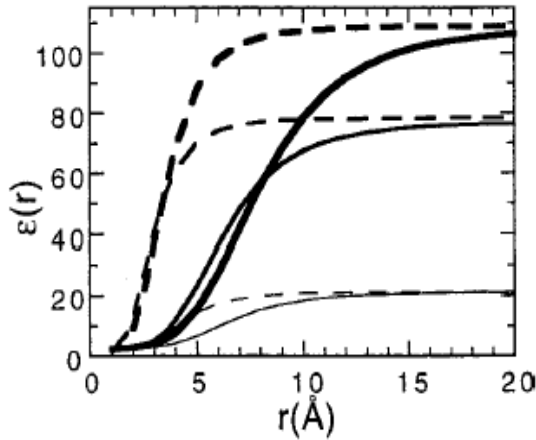
$$\varepsilon(r) = 1 + \frac{4\pi}{3} [\varepsilon(r) + 2] \frac{\alpha}{v} + \frac{2\pi\mu}{\mu_s v} r^3 \varepsilon(r) L \left[ \frac{2\mu\mu_s [\varepsilon(r) + 2]}{(3kT + \mu R(r)) r^3 \varepsilon(r)} \right] \quad (13)$$

In the case of an ion there is no reaction field implications because of the central symmetry of the charge distribution. However, it might happen that local, instantaneous fluctuations of the charge distribution that forms the ion (due mainly to interactions with the neighbor solvent molecules) can result in a local dipolar moment. Therefore, corrections due to reaction field might need to be considered even in this case, and the corrected equation for the dielectric function  $\varepsilon(r)$  was shown to be

$$\varepsilon(r) = 1 + \frac{4\pi}{3} [\varepsilon(r) + 2] \frac{\alpha}{v} + \frac{4\pi\mu}{qv} r^2 \varepsilon(r) L \left[ \frac{q\mu [\varepsilon(r) + 2]}{(3kT + \mu R(r)) r^2 \varepsilon(r)} \right] \quad (14)$$

## Numerical Calculation of dielectric Function in Pure Liquids

Equations (7) and (14) have been solved numerically to obtain  $\varepsilon(r)$  in some common solvents. This was carried out to analyze the dependence of  $\varepsilon(r)$  on



**Figure 1:** Dielectric functions for formamide (thick lines), water (medium), and acetone (thin). Solid lines:  $\varepsilon(r)$  calculated from Eq.(7); dashed lines:  $\varepsilon(r)$  calculated with Eq.(14) that includes the reaction field corrections ( $R(r)$  was calculated with the local approximation derived from Eq.(12))

charge, nature of the solvent and the reaction field corrections. Figure 1 shows dielectric functions for formamide, water and acetone created by a charge  $q=e$ , showing the typical sigmoidal behavior that is characteristic not only of point charge solutes, but also of dipolar sources (taken from Ref.[2]). The effect of the reaction field corrections is to shift the profile towards smaller values of  $r$ . The rate of increase is relatively slow even when reaction field is introduced: for water, e.g., bulk dielectric constant  $\varepsilon_s$  is reached only at a distance  $r \sim 6 \text{ \AA}$  (corrected) and

$r \sim 15 \text{ \AA}$  (uncorrected). A detailed analysis shows that  $\varepsilon(r)$  increases more slowly with distance as the charge of the ion increases: for water, for

example, a change from  $q=e$  to  $q=2e$  lowers the dielectric value from 25 to less than 10 at  $r\sim 5\text{\AA}$ , and from 70 to 50 at  $r\sim 10\text{\AA}$ .

For a dipolar source, the qualitative behavior of  $\epsilon(r)$  is similar to the case of the ion, but the increase of  $\epsilon(r)$  with the distance is much faster than shown in Figure 1. For example, for water, the bulk dielectric is reached at  $r\sim 5\text{\AA}$  for a source dipole  $\mu_s=1\text{D}$ , and  $r\sim 6\text{\AA}$  for  $\mu_s=2\text{D}$ . The effect of increasing the value of  $\mu_s$  on the strength of the dielectric is similar than in the point charge, e.g., in water, an increase from  $\mu_s=1\text{D}$  to  $\mu_s=2\text{D}$  results in a decrease of  $\epsilon(r)$  from 60 to 40 at  $r\sim 3\text{\AA}$ .

### **Energetic of Ion Solvation**

When an ion is immersed in a polar/polarizable solvent like water it polarizes the medium and creates sigmoidal dielectric profiles as discussed above. Since the dielectric is not constant, the original Born approximation is adapted for this inhomogeneous case described by the LDS theory:

$$\Delta G = -\frac{q^2}{2} \left[ \frac{1}{R} - \int_R^\infty \frac{dr}{r^2 \epsilon(r)} \right] \quad (15)$$

where  $R$  is the lower limit of integration. If the usual form of the Born equations is to be used, an effective Born radius  $R_{eff}$  has to be defined such that

$$\Delta G = -\frac{q^2}{2R_{eff}} \left( 1 - \frac{1}{\epsilon_s} \right) \quad (16)$$

Solving Eq.(15) with  $\epsilon(r)$  given by Eq.(14) shows that the difference  $R_{eff} - R$  is positive and decreases as  $R$  increases; moreover, the larger the value of the charge  $q$ , the larger the difference  $R_{eff} - R$  for any given  $R$  (note, then, that if  $R_{eff}$  is independent of the charge  $q$ ,  $R$  must be dependent on the charge).

The fundamentals of the theory outlined above and also its relation with electrostatics in macromolecules is described in details in the following articles:

1. E L Mehler, *The Lorentz-Debye-Sack Theory and Dielectric Screening of Electrostatic Effects in Proteins and Nucleic Acids*, in *Molecular Electrostatic Potential: Concepts and Applications*, J S Murray and K Sen, Editors, Elsevier Science, Amsterdam, pp. 371-405 (1996)
2. S Ehrenson, *Continuum Radial Dielectric Functions for Ion and Dipole Solution Systems*; J. Comp. Chem. **10**, 77 (1989).
3. P Debye, *Polar Molecules*; New York, Dover (1929).

4. P Debye and L Pauling, *The Inter-Ionic Attraction Theory of Ionized Solutes. IV. The Influence of Variation of Dielectric Constant on the Limiting Law for Small Concentrations*. J. Am. Chem. Soc. **47**, 2129 (1925).
5. H A Lorentz, *Theory of Electrons*; New York, Dover (1952)
6. V H Sack, *The Dielectric Constant of Electrolytes*; Phys. Z. **27**, 206 (1926)
7. V H Sack, *The Dielectric Constants of Solutions of Electrolytes at Small Concentrations*; Phys. Z. **28**, 199 (1927).
8. L Onsager, *Electric Moments of Molecules in Liquids*; J. Amer. Chem. Soc. **58**, 1486 (1936).
9. C J F Böttcher, *The Dielectric Constant of Dipole Liquids*; Physica **V**, 635 (1938)